(12) UK Patent Application (19) GB (11) 2 056 874 A

(54) **Hydroformylation of olefinic compounds**

(57) In hydroformylating an olefinic compound in an organic solvent and in the presence of a rhodium complex and a trisubstituted phosphine to give the corresponding aldehyde, a diphosphino compound of the general formula:
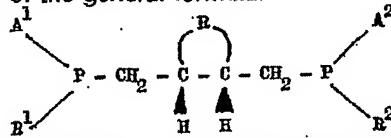
in which each of A^1 and A^2 is an aryl group; each of R^1 and R^2 is an aryl group or a saturated hydrocarbon residue; and
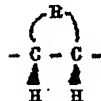
is a substituted or unsubstituted alicyclic hydrocarbon group containing 3 to 6 carbon atoms in the main ring, is added to the reaction system in a proportion of 0.20 to 5.0 equivalents per rhodium atom in the rhodium complex.

The addition of the diphosphino compound has a remarkable life-prolonging effect on the rhodium catalyst.

SPECIFICATION

Hydroformylation of olefinic compounds

5 This invention relates to the hydroformylation of olefinic compounds.
   It is known that hydroformylation can be conducted by reacting an olefin, e.g. ethylene, propylene or butene, with a gaseous mixture of hydrogen and carbon monoxide in an organic solvent and in the presence of a rhodium complex and a trisubstituted phosphine to obtain an aldehyde containing one more carbon atom than the starting olefin. The reaction has been
10 commercially utilized for example in the production of butyraldehyde from propylene. U.S. Patent No. 4,139,565 states that if a hydroformylation reaction is conducted in the co-presence of a rhodium catalyst and a diphosphino compound such as trans-1,2-bis(diphenylphosphinome-thyl)cyclobutane, satisfactory results as to reaction rate and selectivity are obtained even without using a trisubstituted phosphine such as triphenylphosphine and that therefore such a
15 diphosphino compound is useful as a substitute for a trisubstituted phosphine.
   The rhodium complex as used for catalysing the hydroformylation reaction is suited for industrial practice in that it helps perform the reaction under considerably milder conditions, i.e. lower temperature and pressure, than does a cobalt catalyst and that it contributes to a higher selectivity for n-aldehyde. However, since the rhodium complex is quite expensive, the industrial
20 value of a hydroformylation reaction with this complex depends largely on the catalyst life of the complex. The procedure of U.S. Patent No. 4,139,565 does not prolong the life of the catalyst, rather the contrary, and selectivity to n-aldehyde is unsatisfactory.
   However, much research has already been done and many proposals made in connection with means of maintaining the activity of the catalyst for an extended time under hydroformylation
25 conditions. These methods may be roughly classified into three categories:
   (1) The contemplated reaction is carried out while various reaction conditions, such as the concentrations of the rhodium catalyst and trisubstituted phosphine, the partial pressure of carbon monoxide and the reaction temperature, are controlled each within a defined range so as to suppress thermal degradation of the rhodium complex and formation of an inactive highly-
30 carbonylated rhodium complex (e.g. German Patent Application DTOS 2,715,685).
   (2) A small amount of oxygen is allowed to be present in the reaction system (e.g. DTOS 2,730,527).
   (3) The reaction is carried out while the concentration of poisonous high-boiling byproducts in the reaction system is maintained below a certain level (e.g. British Patents Nos. 1,338,237
35 and 1,545,706).
   These previously proposed methods, however, have room for improvement when industrial application is envisaged. The first method (1) is commercially disadvantageous in that the drop of reaction temperature and the increase in concentration of the trisubstituted phosphine result in a reduced reaction rate which would require use of the expensive rhodium catalyst in an
40 increased concentration in order to compensate for the reduction of reaction rate. As regards the second method (2), the trisubstituted phosphine and the end product aldehyde are unstable to oxygen and tend to be converted to the substituted phosphine oxide and organic carboxylic acid, respectively, with the result that not only is the catalyst activity reduced but also undesirable secondary reactions of the product aldehyde are induced. The third method (3) is disadvanta-
45 geous in that maintaining the concentration of high-boiling byproducts acting as catalyst poisons below a certain level is industrially equivalent to frequent regeneration, activation and recovery of the rhodium catalyst, which are of necessity accompanied by losses of the rhodium catalyst and trisubstituted phosphine. Even by the above methods, a depression of catalyst activity is frequently encountered during the reaction and it has been essential to carry out the
50 regeneration, activation and recovery of the rhodium catalyst fairly often. This not only means a complicated procedure but also entails losses of the rhodium catalyst and trisubstituted phosphine in the regeneration step. Thus, the conventional methods for maintaining the activity of the rhodium catalyst have much room for improvement.
   In the published specification of our prior UK Patent Application No. 2,014,138 is claimed a
55 process for producing aldehydes comprising hydroformylating a lower olefin in an organic solvent in the presence of a rhodium complex, from 10 to 500 equivalents of a trisubstituted phosphine per atom of rhodium, and from 0.20 to 2.5 equivalent, per gram atom of the rhodium present in the rhodium complex, of a diphosphinoalkane represented by the general formula:

60

$$A^1 \qquad A^2$$
$$P \!\!-\!\! Z \!\!-\!\! P$$
$$R^1 \qquad R^2$$
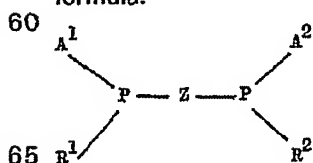
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in which each of A^1 and A^2, which are the same or different, is aryl, each of R^1 and R^2, which are the same or different, is aryl or a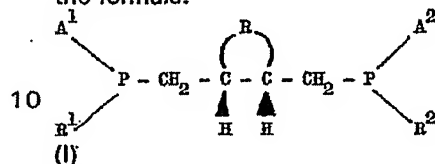 saturated hydrocarbon residue, and Z is alkylene whose principal chain contains 2 to 5 carbon atoms and optionally may have one or more lower alkyl substituents.

5   The present invention is based on the further discovery that when a diphosphino compound of the formula:

$$\underset{R^1}{\overset{A^1}{\diagdown}} P - CH_2 - \overset{B}{\overset{\frown}{\underset{\underset{H}{\blacktriangle}}{C}}} - \overset{}{\overset{}{\underset{\underset{H}{\blacktriangle}}{C}}} - CH_2 - P \underset{R^2}{\overset{A^2}{\diagup}}$$

10

(I)

in which each of A^1 and A^2 is an aryl group; each of R^1 and R^2 is an aryl group or a saturated hydrocarbon and

15

$$- \overset{\overset{R}{\frown}}{\overset{}{\underset{\underset{H}{\blacktriangle}}{C}}} - \overset{}{\overset{}{\underset{\underset{H}{\blacktriangle}}{C}}} -$$
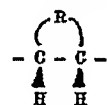
20   is a substituted or unsubstituted alicyclic hydrocarbon group containing 3 to 6 carbon atoms in the main ring, is used as the diphosphinoalkane to be added in combination with a trisubstituted phosphine, the active life of the rhodium catalyst is significantly prolonged and, at the same time, the selectivity of the reaction (ratio of formation of normal aldehyde to branched-chain aldehyde) is further increased in some cases.

25   In accordance with the present invention, a process for hydroformylating an olefinic compound in an organic solvent to obtain the corresponding aldehyde comprises treating the said olefinic compound with gaseous carbon monoxide and hydrogen in the presence of a rhodium complex, 10 to 500 equivalents, per gram-atom of rhodium in the rhodium complex, of a trisubstituted phosphine and 0.20 to 5.0 equivalents, per gram-atom of rhodium in the

30   rhodium complex, of a diphosphino compound of the general formula (I) above.

As a result, the normal aldehyde, which is more useful, can be obtained with high selectivity and, moreover, the concentration of substituted phosphine can be lower than the concentration level conventionally used. Accordingly, even when the reaction is conducted at a lower reaction temperature, the reaction rate can be increased without increasing the concentration of the

35   rhodium catalyst. Moreover, the reaction at a reduced temperature suppresses formation of undesirable high-boiling byproducts, with the result that not only is the catalyst activity stabilized for an extended time period but the frequency of catalyst regeneration is reduced so that the loss of rhodium and trisubstituted phosphine in the regeneration step may be minimized.

40   Referring to general formula (I), the aryl groups A^1 and A^2 and the aryl groups mentioned for R^1 and R^2 are preferably such usual aryl groups as phenyl and naphthyl, either unsubstituted or having substituents such as lower alkyl and lower alkoxy that are inert to the reaction, e.g. as in tolyl and xylyl. Examples of saturated hydrocarbon residues for R^1 and R^2 include methyl, ethyl, propyl, butyl pentyl, hexyl, heptyl, octyl and cyclohexyl.

45   The unsubstituted alicyclic hydrocarbon groups include cycloalkylene groups having 3 to 6 membered ring such as cyclopropylene, cyclobutylene, cyclopentylene and cyclohexylene, cycloalkylene groups substituted by at least one alkyl group containing up to 10 carbon atoms, cycloalkylene groups two of whose carbon atoms are linked through an alkylene group containing up to 20 carbon atoms and cycloalkylene groups two of whose adjacent carbon

50   atoms are constituent members of a benzene ring.

The residues

$$\underset{R^1}{\overset{A^1}{\diagdown}} P - CH_2 - \qquad \underset{R^2}{\overset{A^2}{\diagdown}} P - CH_2 -$$

55

and
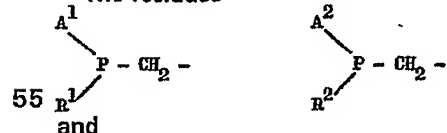
are trans-oriented with respect to the alicyclic hydrocarbon group.

As preferred examples of the diphosphino compound, there may be mentioned trans-1,2-

60   bis(diphenylphosphinomethyl)cyclopropane, trans-1,2-bis(diphenylphosphinomethyl)cyclobutane, trans-1,2-bis(diphenylphosphinomethyl)cyclopentane, trans-1,2-bis(octylphenylphosphinomethyl)-cyclobutane, trans-1,2-bis(diphenylphosphinomethyl)-trans-decahydronaphthalene, trans-2,3-bis(-diphenylphosphinomethyl)bicyclo[2.2.2]octane and trans-9,10-bis(diphenylphosphinomethyl)-9,10-dihydrophenanthrene. Among the above-mentioned groups, trans-1,2-bis(diphenylphosphi-

65   nomethyl)cyclobutane is particularly preferred from the standpoints of availability, catalyst-life-

prolonging effect and chemical stability.

The above-mentioned diphosphino compounds may be used singly or as a mixture of two or more of them.

In the practice of this invention, the diphosphino compound is used in a proportion of 0.20 to
5 5.0 equivalents, preferably 0.25 to 3.5 equivalents, based on each gram-atom of rhodium in the rhodium complex. If the amount of diphosphino compound is less than 0.20 equivalent per gram-atom of rhodium, the addition of the diphosphino compound does not manifest its effect in any substantial measure, while the addition of more than 5.0 equivalents of the diphosphino compound per gram-atom of rhodium is undesirable because it causes a decrease in catalyst
10 activity. The hydroformylation of olefinic compounds on an industrial scale is preferably carried out in a continuous process. Such a reaction is preferably conducted while the diphosphino compound is fed continuously or intermittently so that the concentration of diphosphino compound in the reaction system will be held substantially constant.

In accordance with this invention, it is essential, as aforesaid, to use an excess of a
15 trisubstituted phosphine with respect to the rhodium complex, along with the diphosphino compound. The addition of the trisubstituted phosphine is beneficial to selectivity of reaction (especially, selectivity to n-aldehyde) and catalyst life. The proportion of the trisubstituted phosphine is 10 to 500 equivalents per gram-atom of rhodium in the rhodium complex and, more desirably, 25 to 300 equivalents on the same basis.
20 Many suitable trisubstituted phosphines are known, but in terms of catalyst activity, reaction selectivity and catalyst life, triarylphosphines, triarylphosphites and alkyldiarylphosphines are preferred, more specifically, triphenylphosphine, trinaphthylphosphine, tritolylphosphine, triphenylphosphite and propyldiphenylphosphine.

The rhodium complex may be any rhodium complex capable of catalysing hydroformylation. A
25 large number of such rhodium complexes are known but such rhodium complexes as $HRh(CO)(PR_3)_3$ [where R is alkyl or aryl] and rhodium carbonyl clusters are especially desirable in terms of catalyst activity, solubility and ease of use of the catalyst. As typical examples of such rhodium complexes, there may be mentioned $HRh(CO)[P(C_6H_5)_3]_3$, $HRh(CO[P(C_6H_4CH_3)_3]_3$, $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$.
30 The rhodium complex may be added by preparing a catalyst solution in an independent vessel in the conventional manner and feeding the solution to the hydroformylation reaction vessel.

In the practice of this invention, the concentration of the rhodium complex in the reaction system is preferably in the range 0.05 to 5.0 milligram-atom/litre as rhodium metal. If the concentration level of the rhodium complex is less than 0.05 milligram-atom/litre and especially
35 below 0.025 milligram-atom/litre, the reaction rate is seriously reduced. On the other hand, the use of the rhodium complex at a level exceeding 5.0 milligram-atom/litre is not only uneconomical but also causes a reduction of catalyst life.

The olefinic compounds to which the method of this invention is applicable are those containing up to 6 carbon atoms, such as ethylene, propylene, 1-butene, isobutene, 1-pentene,
40 1-hexene, allyl alcohol and allyl methyl ether.

The organic solvent may be any solvent that is capable of dissolving the rhodium complex, trisubstituted phosphine and diphosphino compound and that will not interfere with hydroformylation. For industrial operations, it is economically advantageous to use the product aldehyde or its condensation byproducts. Other suitable solvents include aromatic hydrocarbons such as
45 benzene, toluene, xylene and dodecylbenzene, alicyclic hydrocarbons such as cyclohexane, ethers and esters.

The hydroformylation reaction according to this invention is carried out by feeding carbon monoxide gas and hydrogen gas into an organic solvent containing the rhodium complex, trisubstituted phosphine, diphosphino compound and olefinic compound. It is desirably carried
50 out by a continuous method in a stirring-type reaction vessel or a columnar reaction vessel. The reaction temperature is an important factor because it governs both the reaction rate and catalyst life. The reaction is desirably conducted in the temperature range of 50 to 120°C, and more desirably at 60 to 105°C. At temperatures below 50°C, the reaction rate is too slow, while the catalyst life is too short if the reaction is carried out at temperatures over 120°C.
55 The partial pressure ratio of hydrogen to carbon monoxide is desirably within the range 1:2 to 10:1 in the mixed gas feed. In order to attain an adequate reaction rate, an adequate reaction selectivity and a sufficiently long catalyst life, it is important to ensure that, during the progress of reaction, the absolute partial pressure of carbon monoxide in the reaction system lies somewhat between 0.1 and 2.5 bars. When the absolute partial pressure of carbon monoxide is
60 higher than 2.5 bars, the relative yield of branched aldehyde is increased and the catalyst life is shortened. Where the olefinic compound is gaseous at atmospheric temperature and pressure, it is industrially advantageous to ensure that the total pressure of olefin, hydrogen and carbon monoxide will be 5 to 30 bars.

The reaction system may include other gases inert to hydroformylation, such as nitrogen,
65 helium, argon, methane, ethane, propane and butane.

The aldehydes produced by the above reaction can be separated from the reaction mixture by procedures known *per se*. The aldehydes with comparatively low boiling points are mainly taken out from the reaction system along with the off gas, while high-boiling aldehydes are separated by depressurizing the dissolved gas and subjecting it to distillation.

5   Water-soluble aldehydes, e.g. hydroxybutyraldehyde, which is obtainable by hydroformylation of allyl alcohol, can be advantageously extracted with an aqueous extractant.

This invention will be further described by way of the following Examples. In the Examples and Comparative Examples, the reaction was invariably conducted in a one-litre stainless steel autoclave equipped with a magnetic stirrer, thermometer, gas inlet and gas outlet.

10

EXAMPLE 1

The autoclave was charged with a mixture of 150 ml of *n*-butyraldehyde and 250 ml of dioctyl phthalate containing as dissolved 0.60 millimole of $HRh(CO)(PPh_3)_3$ (Ph = phenyl), 40 millimoles of triphenylphosphine and 0.60 millimole of *trans*-1,2-*bis*(diphenylphosphinomethyl)-

15 cyclobutane. The autoclave was sufficiently purged with hydrogen/carbon monoxide gas mixture (molar ratio, 2:1) and the internal temperature was maintained at 85°C. Then, propylene, carbon monoxide, hydrogen and nitrogen gases were introduced from the gas inlet at the flow rates of 30 litres/hour, 20 litres/hour, 40 litres/hour and 140 litres/hour, respectively, and the reaction gas was purged so that the internal pressure of the autoclave was held

20 at 15 bars absolute by means of a pressure-regulating valve provided in the gas outlet tube. The product butyraldehydes (isobutyraldehyde and *n*-butyraldehyde) were continuously withdrawn from the reactor along with the off gas. It was confirmed with a level gauge fitted to the autoclave that the volume of liquid in the reactor was constant after a steady state had been established. The gas emerging from the reactor was bubbled into, so as to ensure thorough

25 contact with, toluene cooled with solid carbon dioxide and acetone, and the product butyraldehydes were trapped and analysed by gas chromatography. The gas emerging from the reactor was also analysed by gas chromatography to determine the proportions of carbon monoxide, hydrogen, propylene and propane in the emergent gas.

Table 1 shows the rates of formation of *n*-butyraldehyde and isobutyraldehyde at 20 hours

30 and 170 hours after the start of the reaction. The fact that the rate of formation of butyraldehyde after 170 hours of reaction was substantially equal to that after 20 hours indicates that the catalyst activity had been sustained without any significant decrease throughout the reaction.

35 *EXAMPLE 2*

The reaction procedure described in Example 1 was repeated except that 0.90 millimole of *trans*-1,2-*bis*(diphenylphosphinomethyl)-cyclobutane was used. Table 1 shows the rates of formation of *n*-butyraldehyde and isobutyraldehyde at 20 hours and 170 hours after the start of the reaction.

40

EXAMPLE 3

The reaction procedure described in Example 1 was repeated except that 0.75 millimole of $HRh(CO)(PPh_3)_3$, 50 millimoles of triphenylphosphine and 0.90 millimole of *trans*-1,2-*bis*(diphenylphosphinomethyl)cyclopentane were used. Table 1 shows the rates of formation of *n*-

45 butyraldehyde and isobutyraldehyde after 20 hours and 170 hours of reaction.

EXAMPLE 4

A mixture of 100 ml of propionaldehyde and 300 ml of dioctyl phthalate, in which 0.15 millimole of $Rh_6(CO)_{16}$, 90 millimoles of triphenylphosphine and 0.6 millimole of *trans*-1,2-

50 *bis*(diphenylphosphinomethyl)cyclobutane were dissolved, was used as a catalyst solution and the internal temperature of the reactor was maintained at 70°C. As in Example 1, ethylene, carbon monoxide, hydrogen and nitrogen gases were introduced at the rates of 45 litres/hour, 30 litres/hour, 60 litres/hour and 85 litres/hour, respectively, and the internal pressure of the reactor was kept at 13 bars. The rates of formation of propionaldehyde at 20 hours and 170

55 hours after the start of the reaction were 0.991 mole and 0.980 mole, respectively, per hour.

COMPARATIVE EXAMPLE 1

The reaction procedure of Example 1 was repeated except that *trans*-1,2-*bis*(diphenylphosphinomethyl)cyclobutane was not added at all.

60 Table 1 shows the rates of formation of *n*-butyraldehyde and isobutyraldehyde at 20 and 170 hours after the start of the reaction. It will be apparent that, compared with the results obtained in Example 1, the rate of formation of aldehyde was significantly low and that the ratio of *n*-aldehyde to the total product andehyde was low.

65 *COMPARATIVE EXAMPLE 2*

The reaction procedure of Example 1 was repeated except that triphenylphosphine was not added at all. Gas-chromatographic determinations of carbon monoxide and propylene in the emergent gas showed that the progress of reaction was very fast in a period immediately following the start of the reaction, but that due to a marked decrease of catalyst activity, the
5 rates of formation of n-butyraldehyde and isobutyraldehyde after 20 hours of reaction were as   5
low as 0.389 mole/hour and 0.108 mole/hour, respectively.

It is obvious that, compared with the results of Example 1, the omission of trisubstituted phosphine resulted in a marked decrease of catalyst activity and a low relative yield of n-butyraldehyde.
10   10

COMPARATIVE EXAMPLE 3

The reaction procedure of Example 1 was repeated except that 0.06 millimole of trans-1,2-bis(diphenylphosphinomethyl)cyclopentane was used. Table 1 shows the rates of formation of n-butyraldehyde and isobutyraldehyde at 20 and 170 hours after the start of the reaction.
15   15

COMPARATIVE EXAMPLE 4

The reaction procedure of Example 1 was repeated except that 6.0 millimoles of trans-1,2-bis(diphenylphosphinomethyl)cyclobutane was used. Table 1 shows the rates of formation of n-butyraldehyde and isobutyraldehyde as 20 hours and 170 hours after the start of the reaction.
20   20

Table 1

	Rates of formation of butyraldehydes (mole/hour)			
	After 20 hours		After 170 hours	
	n-Butyr-aldehyde	Isobutyr-aldehyde	n-Butyr-aldehyde	Isobutyr-aldehyde
Example 1	0.634	0.056	0.627	0.055
Example 2	0.590	0.050	0.581	0.049
Example 3	0.717	0.063	0.694	0.060
Comparative Example 1	0.628	0.067	0.460	0.049
Comparative Example 3	0.619	0.066	0.487	0.052
Comparative Example 4	0.278	0.023	0.269	0.022

EXAMPLE 5

The autoclave was charged with 320 ml of a toluene solution containing 0.60 millimole of
45 HRh(CO)(PPh$_3$)$_3$, 60 millimoles of triphenylphosphine and 0.525 millimole of trans-1,2-bis(di-   45
phenylphosphinomethyl)cyclobutane. The atmosphere in the autoclave was thoroughly purged with nitrogen gas and then with hydrogen/carbon monoxide (molar ratio, 2:1), and the autoclave was heated to a constant temperature of 65°C. Then, a gaseous mixture of hydrogen and carbon monoxide (molar ratio, 2:1) was introduced into the autoclave, and utilizing this gas,
50 the internal pressure was controlled to 3.0 bars absolute and the flow rate of emergent gas to   50
20 n1/hour. By means of a constant-speed pump, a total of 80 ml of allyl alcohol was introduced under stirring at the rate of 40 ml/hour over a period of 2 hours. After the feed of allyl alcohol had been terminated, the reaction was further continued for 2 hours. The emergent gas was thoroughly guided into a toluene trap cooled with solid carbon dioxide and acetone and
55 the accompanying allyl alcohol, propionaldehyde and other low-boiling products were collected   55
in the above toluene trap. The hydroformylation of allyl alcohol was thus conducted at constant pressure and temperature for 4 hours. Gas chromatographic analysis of the reaction mixture and of the liquid in the toluene trap showed that there was 0.035 millimole of unreacted allyl alcohol (conversion of allyl alcohol = 97%). The yields of propionaldehyde, n-propanol, 2-
60 methyl-3-hydroxy-propionaldehyde and 4-hydroxybutyraldehyde were 0.080 mole, 0.034 mole,   60
0.114 mole and 0.856 mole, respectively.

The internal temperature of the autoclave was reduced to the ambient and the autoclave was decompressed. The reaction mixture was then transferred to a one-litre separatory funnel equipped with agitator means, care being exercised to prevent exposure of the mixture to
65 atmospheric air. At room temperature and in a hydrogen gas atmosphere, the unreacted alcohol   65

and reaction products in the reaction mixture were extracted twice with 400 ml of distilled water. The residual toluene solution containing the catalyst components was charged into the autoclave and the hydroformylation of allyl alcohol was conducted as described above for 4 hours. After the reaction, the unreacted allyl alcohol and reaction product were extracted from
5 the reaction mixture. The above procedure was repeated for a total of 10 times. Table 2 shows   5
the yields of propionaldehyde, n-propanol, 2-methyl-3-hydroxypropionaldehyde and 4-hydroxy-butryaldehyde after the 5th and 10th reactions.

TABLE 2

Product	Propion-aldehyde (mole)	n-Propanol (mole)	2-Methyl-3-hydroxy-propionaldehyde (mole)	4-Hydroxy-butyr-aldehyde (mole)
Reaction				
5th	0.078	0.033	0.112	0.840
10th	0.077	0.032	0.111	0.823

EXAMPLE 6

· The autoclave was charged with a dodecylbenzene solution containing 0.80 millimole of $HRh(CO)(PPh_3)_3$, 50 millimoles of triphenylphosphine and 0.80 millimole of trans-1,2-bis(diphenylphosphinomethyl)cyclobutane. The internal atmosphere of the autoclave was thoroughly purged with nitrogen gas and then with hydrogen:carbon monoxide (molar ratio, 3:1), and the
25 internal temperature was elevated to 90°C. At this constant temperature, hydrogen:carbon   25
monoxide gas (molar ratio, 3:1) was introduced into the autoclave, and by utilizing this mixed gas, the internal pressure of the autoclave was controlled to 3.0 bars absolute and the flow rate of emergent gas to 20 N1/hour. By means of a constant-speed pump, 90 ml of 1-pentene was introduced under stirring at the rate of 45 ml/hour over a period of 2 hours. After the
30 introduction of 1-pentene was terminated, the reaction was further continued for 2 hours. The   30
emergent gas was bubbled into, so as to ensure thorough contact with, toluene cooled with solid carbon dioxide and acetone and the accompanying 1-pentene and reaction products were thus collected in the trap. The hydroformylation of 1-pentene was thus carried out at constant temperature and pressure for 4 hours. Gas-chromatographic analysis of the reaction mixture and
35 of the liquid in the toluene trap revealed that there was 0.041 mole of unreacted 1-pentene   35
(conversion of 1-pentene, 95%). The yields of n-pentane, 2-pentene, 2-methylpentanal and n-hexanal were 0.0151 mole, 0.0312 mole, 0.0547 mole and 0.679 mole, respectively.

The autoclave was decompressed while the internal temperature was reduced to 50°C, and at this temperature distillation was carried out for about 1 hour while the degree of depressuriza-
40 tion was varied according to the distillation rate. The residual dodecylbenzene solution   40
containing the catalyst components was charged into the autoclave and the hydroformylation of 1-pentene was carried out in the same manner as described above for 4 hours. The unreacted 1-pentene and reaction products were separated after the reaction. The above procedure was repeated for a total of 10 times. Table 3 shows the yields of unreacted 1-pentene and various
45 reaction products after the 5th and 10th reactions.   45
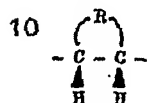
TABLE 3

	Unreacted 1-pentene (mole)	n-Pentane (mole)	2-Pentene (mole)	2-Methyl-pentanal (mole)	n-Hexanal (mole)
5th	0.0535	0.0153	0.0307	0.0538	0.668
10th	0.0715	0.0200	0.0225	0.0528	0.653

CLAIMS

1. A process for hydroformylating an olefinic compound in an organic solvent to obtain the corresponding aldehyde, that comprises treating the said olefinic compound with gaseous
60 carbon monoxide and hydrogen in the presence of a rhodium complex, 10 to 500 equivalents,   60
per gram-atom of rhodium in the rhodium complex, of a trisubstituted phosphine and 0.20 to 5.0 equivalents, per gram-atom of rhodium in the rhodium complex, of a diphosphino compound of the general formula:
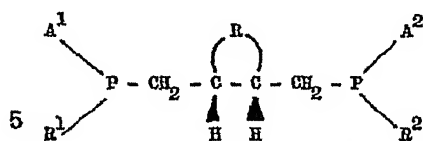
in which each of A¹ and A² is an aryl group; each of R¹ and R² is an aryl group or a saturated hydrocarbon residue; and

is a substituted or unsubstituted alicyclic hydrocarbon group containing 3 to 6 carbon atoms in the main ring.

2.   A process as claimed in claim 1 in which the concentration of the rhodium complex in the reaction system is 0.05 to 5.0 milligram-atom/litre as rhodium metal.

3.   A process as claimed in claim 1 or 2 in which the rhodium complex is a compound of the general formula $HRh(CO)(PR_3)_3$ (where R is alkyl or aryl) or a rhodium carbonyl cluster.

4.   A process as claimed in claim 3 in which the rhodium complex is $HRh(CO)[P(C_6H_5)_3]_3$, $HRh(CO)[P(C_6H_4CH_3)_3]_3$, $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$.

5.   A process as claimed in any preceding claim in which the olefinic compound contains up to 6 carbon atoms.

6.   A process as claimed in claim 5 in which the olefinic compound is ethylene, propylene, 1-butene, isobutene, 1-pentene, 1-hexene, allyl alcohol or allyl methyl ether.

7.   A process as claimed in any one of claims 1 to 6 in which the diphosphino compound is trans-1,2-bis(diphenylphosphinomethyl)cyclobutane.

8.   A process as claimed in any one of claims 1 to 6 in which the diphosphino compound is trans-1,2-bis(diphenylphosphinomethyl)-cyclopropane, trans-1,2-bis(diphenylphosphinomethyl)-cyclopentane, trans-1,2-bis(octylphenylphosphinomethyl)-cyclobutane, trans-1,2-bis(diphenyl-phosphinomethyl)-trans-decahydronaphthalene, trans-2,3-bis(diphenylphosphinomethyl)-bicyclo[2.2.2]octane or trans-9,10-bis(diphenylphosphinomethyl)-9,10-dihydrophenanthrene.

9.   A process as claimed in any preceding claim in which the trisubstituted phosphine is a triarylphosphine, triarylphosphite or alkyldiarylphosphine.

10.   A process as claimed in claim 9 in which the trisubstituted phosphine is triphenylphosphine, trinaphthylphosphine, tritolylphosphine, triphenylphosphite or propyl-diphenylphosphine.

11.   A process as claimed in any preceding claim in which the diphosphino compound is used in a proportion of 0.25 to 3.5 equivalents per gram-atom of rhodium in said rhodium complex.

12.   A process as claimed in any preceding claim in which the hydroformylation of said olefin is carried out at a reaction temperature of 50 to 120°C.

13.   A hydroformylation process as claimed in any preceding claim in which the partial pressure ratio of hydrogen and carbon monoxide is 1:2 to 10:1 as the feed mixed gas.

14.   A process as claimed in claim 13 in which the absolute partial pressure of carbon monoxide in the reaction system is 0.1 bar to 2.5 bars.

15.   A process as claimed in any preceding claim in which the organic solvent is the product aldehyde, a condensation product thereof, or an aromatic hydrocarbon, alicyclic hydrocarbon, ether, ketone or ester.

16.   A process as claimed in claim 1 carried out substantially as hereinbefore described in any one of Examples 1 to 6.

17.   Aldehydes produced by a process as claimed in any one of the preceding claims.